

National Bureau of Standards



TECHNICAL NEWS BULLETIN

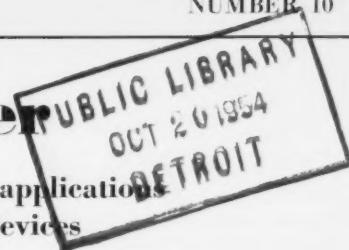
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Diode Amplifier

semiconductor amplifier offers important applications
in computers and other electronic devices



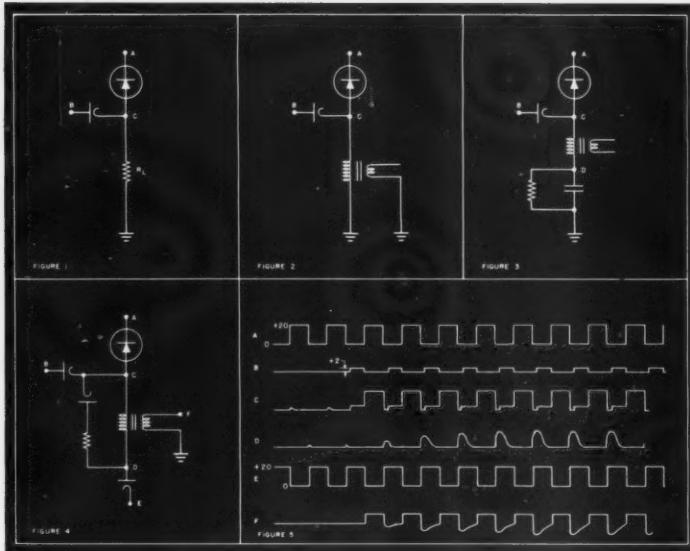
RESEARCH on application of semiconducting diodes has led to the development of a new class of amplifiers that utilizes the reverse transient phenomenon of these two-element rectifying devices. Devised by A. W. Holt of the National Bureau of Standards, the diode amplifier—using no vacuum tubes and achieving power gains up to 10 per stage—promises important application in the future design of high-speed electronic digital computers. For example, it may be used as a pulse repeater stage, in varied types of flip-flop circuits, or as a wide-band, flat-response amplifier. Because suitable diodes are now in regular production, commercial applications are practical at the present time. Future improvement in the manufacture of diodes may make the principle useful for amplification at even microwave frequencies.

From a material standpoint the device requires a semiconducting crystal which exhibits a large degree of carrier storage. Such carrier storage characteristics have been studied at NBS since 1951, primarily by J. H. Wright. In order to operate the diode as an amplifier it must be supplied with power from an r-f source whose frequency is the same or higher than the modulating signal frequency. This requirement puts the circuit in the same category as magnetic and dielectric amplifiers.

A semiconductor diode of the germanium or silicon

type has two static conditions: (1) a forward conducting state, characterized by high conductivity, and (2) a reverse conducting state, characterized by low conductivity. The forward state is achieved by applying a biasing voltage so that the anode is more positive than the cathode; the reverse state is achieved by applying voltage of opposite polarity. The forward voltage acts to create a steady supply of "carriers" of current within the semiconducting material, thus maintaining a condition of high conductivity. Carriers are not created during the reverse static state. If the voltage applied to the diode is switched quickly from forward to reverse voltage, a transient phenomenon occurs in which a large reverse current flows for an appreciable time after switching takes place, and decays until the static reverse state is reached. The transient current occurs because the carriers which were present due to the forward voltage remain available to be swept out by the application of the reverse voltage. The carriers do not remain indefinitely during a period of delay between cessation of forward voltage and application of reverse voltage; instead, their number decreases with time during this period.

Although amplification in the diode is not a continuous phenomenon, the action may be likened to the way in which amplification is obtained in a transistor. In a transistor, the emitter can be regarded as a diode



Basic diode amplifier circuit developed at NBS. Figure 1, input signal is at B, output is at C, clock power is applied to point A. Figure 2, similar in operation to figure 1, this circuit, the transformer-diode-coupled amplifier, provides current gain by use of a transformer. Figure 3, the addition of a capacitor and resistor between the transformer and ground aids in transformer primary recovery between pulses, on a many-pulse basis. Figure 4, an improvement on the circuit of figure 3 which permits the transformer to recover on a pulse-to-pulse basis is achieved by driving point E with a clock voltage 180 degrees out of phase with the power supply clock. Figure 5, waveforms at various points in the circuit of figure 4, clock (A) is shown here as a square wave although a half-wave rectified sine wave can also be used. (B) and (F) are respectively input and output signals.

existing in the forward conducting state, and the collector as a diode in the reverse state. If any of the carriers created by the forward biased diode are transported to the vicinity of the reverse biased diode, a larger current than the static current will flow in the latter diode.

Voltage on the emitter of a transistor produces current which creates carriers. These carriers change the current in the collector, which in turn changes the voltage across the collector. In the case of a junction transistor used in the common base circuit, the collector current is almost equal to the emitter current, so that power gain is effectively determined by the ratio between the forward and the reverse resistances. Thus, power gain is obtained by a transfer of current from one circuit of low impedance to another circuit of high impedance.

The diode amplifier obtains its power gain in a similar manner, except that one electrode serves as both emitter and collector, but at different times. During one-half of the cycle, the anode is more positive than the cathode, and the anode acts as the emitter of the junction transistor; during the other half-cycle, the anode acts like a collector. When it is an emitter, it injects carriers into the germanium with only a small applied forward voltage—i. e., at a low impedance level. When it is a collector, the anode withdraws these same carriers, but only by applying a much higher voltage—at a higher impedance level.

Resistance-Diode-Coupled Amplifier

The simplest form of diode amplifier is the resistance-diode-coupled circuit (fig. 1). The waveform applied to point A is from a one-megacycle power source. This frequency was chosen for experimental purposes because its one-microsecond period is approximately

equal to the decay time of the carriers in the diodes which have been most extensively used. The r-f supply, or "clock", not only acts as the power source but also as the switch which controls the two separate phases of the amplification cycle: the intake of signal power into the amplifier diode (injection of carriers) and the output of amplified power (decay of carriers). As an analogy, the operation of the diode amplifier may be likened to that of a gasoline engine, where fuel is injected during one part of the cycle and fired at a later part of the cycle.

When there is no input at point B, there is no output because of the high impedance of the amplifier diode. A small voltage spike does appear in the output due to the small capacitance of the diode. This, however, can be decreased by paralleling the load resistor with a capacitor for capacitance division. When point B is raised to plus 2 volts while the clock is at zero volts, carriers are injected into the diode by current in the direction B-C-A. The diode then presents for a short time a very low impedance to the reverse voltage that the clock applies. Since this impedance is low compared to the load resistor, most of the clock voltage appears across the resistor.

Power gains of about 10 (average output divided by average input) have been measured using a 20-volt clock. The only limitation on the amplitude of the clock voltage is that it not exceed the reverse breakdown voltage. The requirement on the clock supply is rather severe in that during the time that the clock is at zero volts, its impedance should be very low, so that as much as possible of the available input signal power will be across the diode and not divided between the diode and the clock source. In practical applications, the clock voltage may be distributed as a full sine wave and then half-wave rectified near the point of use.

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Transformer-Diode-Coupled Amplifier

Some circuit element which transforms voltage gain to current gain is essential to most of the circuits using the diode amplifier, because there is no average current gain in the diodes that have been used so far in the experiments performed at the Bureau. The transformer-diode-coupled circuit shown in figure 2 achieves current gain through a step-down transformer. Its operation is similar to the resistance-diode-coupled amplifier. The circuit in this form is suitable for the amplification of low-duty-cycle pulses but will not operate at high duty cycles because the stored energy in the magnetic circuit will not permit the transformer primary to "recover" or "flyback". A solution to this difficulty is obtained through the addition of a capacitor and resistor between the transformer primary and ground, as shown in figure 3. This circuit has the disadvantage that the flyback requirements of the inductance are satisfied only on a many-pulse basis and not on a pulse-to-pulse basis. The many-pulse average can also cause trouble in turning off the stage at the end of a train of pulses.

If the end of the transformer primary (point E, fig. 4) were to be driven by a clock voltage 180 degrees out of phase with the power supply clock, the flyback requirements would be satisfied on a pulse-to-pulse basis because the point D would be allowed to fly back or not as necessary. During the time the clock pulse is on and when point A is up, point E is at ground and conventional current flows through the path A-C-D-E. After the power clock pulse, point E is driven positive by the other clock phase, disconnecting the diode between D and E. At this same time, point B may be charging the diode amplifier for the next power clock pulse. The series diode and resistor between C and D provide critical damping of the flyback.

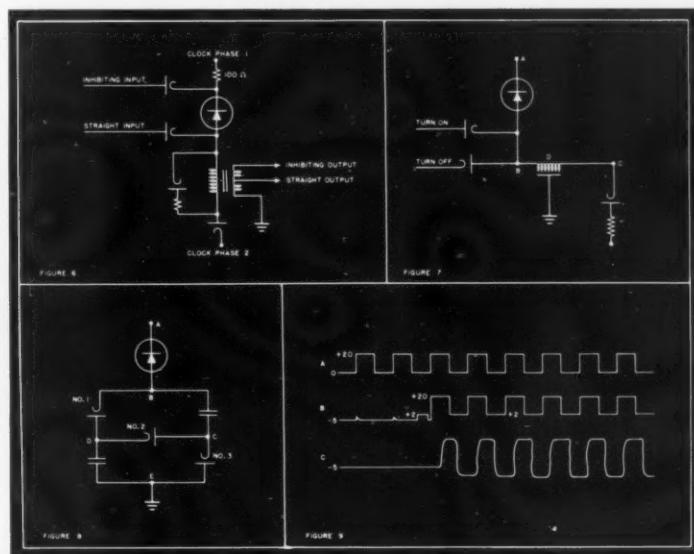
Pulse Repeater Stage

Further development of the diode-amplifier concept leads to the design of a complete "pulse repeater stage" for application in electronic digital computers. The circuit shown in figure 6 satisfies the essential requirements for a computer stage. It is a combination of the transformer-diode-coupled amplifier (fig. 4) and an inhibiting gate. Extra logical "or" gates may be added as desired. Delay lines may be used but can be avoided in most cases, since the carriers in the amplifier diode store information. It may be necessary, however, to use some delay lines to time accurately the inhibiting pulses.

Flip-Flop Circuits

The diode amplifier can be used as the basis for a variety of "dynamic" flip-flop circuits—oscillators which can remain stable either in an oscillating or a nonoscillating state. The circuit shown in figure 7 stores energy between clock pulses in a delay line. The oscillating state is started by raising point B to plus 20 volts to inject carriers. On the clock pulse immediately following, point B is raised to plus 20 volts, and the pulse travels down the delay line. At point C it sees an open circuit and so is returned in the same polarity at the proper time to inject more carriers into the amplifier diode. The delay line serves as an impedance-matching device as well as a delay line, for it can provide the necessary current. In injecting carriers into the amplifier diode, however, the delay line sees a very low impedance, and so some energy is returned down the line for a third travel, negative this time. At point C, however, the negative pulse is matched and absorbed; if it were not absorbed, it would travel back down the line a fourth time and prevent the next carrier injection.

Computer pulse repeater stage, figure 6, which uses the NBS diode amplifier. Additional logical "or" gates may be added as desired. Figure 7, flip-flop circuit stores energy between clock pulses in the delay line (D). Figure 8, current-doubler flip-flop circuit. Condensers are charged in series and discharged in parallel. Figure 9, waveforms of the circuit in figure 8.



Another flip-flop circuit, shown in figure 8, is a current-doubler type. Essentially, it charges two capacitors in series and then discharges them in parallel. If point B is pulled positive, diodes Nos. 1 and 3 are cut off; and current flows through the path B-C-D-E, thus charging the two capacitors in series. When point B becomes negative, diode 2 is cut off, and current flows through the paths E-D-B and E-C-B, thus discharging the capacitors in parallel. When used with the germanium diode amplifier, this circuit makes a flip-flop whose applied frequency can be varied over a very wide range. Many other flip-flop circuits have been developed, some of which are even simpler and less expensive than these described here.

Higher-Speed Circuitry

Silicon junction diodes have a much faster transient recovery than germanium junction diodes, and can be used in faster circuits. In experiments carried out at NBS to study the usefulness of the silicon diode as a diode amplifier, a current-doubler type of flip-flop operated satisfactorily with a clock frequency of 25 megacycles; the circuit exhibited start-stop times of about 100 millimicroseconds. It should be possible to achieve much higher frequencies by using diodes with even shorter decay times. This promises to provide very fast, practical circuitry for future use in electronic computers and many other useful applications as well.

Portable Air Infiltration Meter

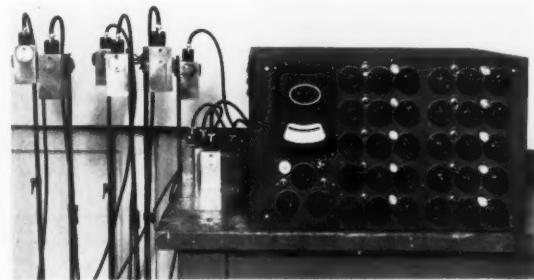
A PORTABLE air infiltration meter designed by C. W. Coblenz of NBS provides an improved means for determining the rate of air infiltration between different rooms of a building and the outside.

In the past, precise infiltration measurements have been restricted to laboratory installations because the equipment was cumbersome. However, the NBS instrument, being portable and compact, lends itself well to field investigations. It can be employed for tests in buildings without greatly inconveniencing the occupants and is expected to be of value in obtaining more comprehensive and precise data on that part of heating and air conditioning loads incident to infiltration in buildings.

Using a method developed by W. G. Marley of England, the change in concentration of a tracer gas, due to infiltration of outside air, is measured as an index of the air change rate. Since it has been shown that the number of air changes occurring during a given time is equal to the natural logarithm of the ratio of the tracer gas concentration at the beginning and at the end of the time interval, absolute concentration measurements are unnecessary. Only the percentage change in concentration need be measured, and this can be determined readily by noting the change in thermal conductivity of the tracer gas-air mixture as the test progresses.

It was found that helium is very satisfactory as a tracer gas because of its high thermal conductivity compared to air. Small changes in helium concentration result in significant changes in thermal conductivity of the helium-air mixture which can be measured with sufficient accuracy using relatively simple instrumentation.

In each probe of the Bureau's meter are two matched and equally heated thermistors, which are connected to form two legs of a Wheatstone bridge circuit. They are installed in identical cylindrical cavities of a metal



Infiltration meter with metal probes and console.

block to provide equivalent heat-absorbing surfaces. One cavity is air-filled and hermetically sealed while the other has small holes at the top and the bottom. This cavity is continuously ventilated through the holes by natural convection induced by the heated thermistor. Since the thermal conductivity of helium is about six times that of air, the thermistor in the ventilated cavity will be cooler than the other by an amount dependent on the quantity of helium "contaminating" the air.

The resulting change in the temperature of the thermistor causes an inverse change in its resistance. Thus any significant change in helium concentration, due to infiltration of outside air into the room under observation, unbalances the Wheatstone bridge circuit, and the effect can be read directly on a microammeter.

A practically constant heating current for the thermistors is obviously essential and, to obtain it, a variable transformer is used on the a-c side of a full-wave selenium rectifier. This transformer is manually adjusted to compensate for changes in line voltage, and in the d-c voltage caused by aging of the rectifier, and for variation in voltage drop across the rectifier resulting from use of a different number of probes during each test. Fluctuations in the line voltage after the adjustment is made are compensated for by using a voltage regulator tube in each probe circuit and by employing a variable resistance tube as the series resistor for the voltage regulator tube. With this combination, line voltage variations ranging from 70 to 120 volts cause

less than 0.4 percent change in the thermistor current.

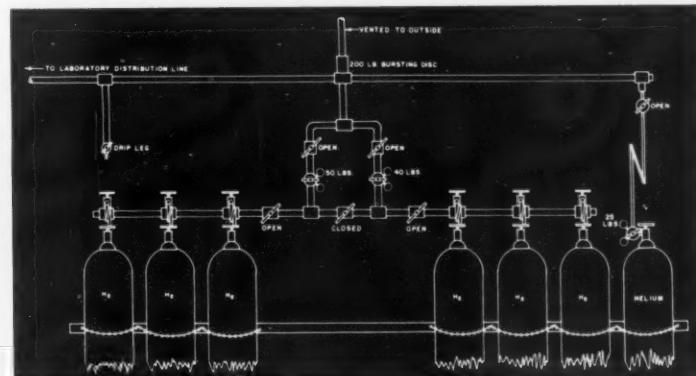
The assembly is designed to simultaneously accommodate ten probes connected to one console. By use of a multiposition gang switch, it is possible to observe the changes in helium concentration in ten different rooms or areas during one test.

For infiltration measurements, the console is placed at a central location in the building under study, and a probe is mounted on a tripod near the middle of each room several feet above the floor. The probes are connected to the console cabinet by means of cables. After adjusting the heating current, at least one-half hour is allowed for all components to warm up to a steady-state condition. Next, the bridge circuits are

balanced by adjusting the balancing resistors so that the meter reads zero in each case. Helium, in the amount of approximately one-half of one percent of the total volume of the space, is then introduced directly into the rooms. Thorough mixing is obtained either by use of desk-type fans or, when available, by means of a forced-air heating system.

Readings are taken from all probes used for the test at intervals of 3 to 15 minutes, depending on the rate of air change. A careful investigation indicates that the meter readings vary linearly with the helium concentrations, and that the accuracy is ample for present purposes, at concentrations less than one-half of one percent of helium in air.

Safety Installation for Hydrogen Distribution Lines



A typical installation showing two banks of hydrogen tanks and the helium safety tank connected through a pressure-reducing network. Helium begins to flow only if the hydrogen line pressure drops to the regulated pressure of the helium. Hydrogen remaining in the system is then replaced by the inert helium.

THE USE OF HYDROGEN GAS in heat-treating and brazing processes is a standard laboratory practice which presents an inherent explosion hazard, especially if the gas is supplied from a remote reservoir and piped to the various operating stations. One general practice is to allow hydrogen to flow into an enclosure (such as a bell jar) and escape into the room. Safe operation depends on the hydrogen being above atmospheric pressure and maintaining a continuous outward flow. If the hydrogen pressure is allowed to fall below that of the atmosphere, air and hydrogen will mix. When about 7 to 73 percent of hydrogen is in the mixture, an explosion can occur if the temperature in the operating chamber is at approximately 500 to 600 degrees C. While there are differential pressure controls and relay devices commercially available which automatically indicate a pressure change, these devices will not prevent an explosion from occurring within the operating chamber.

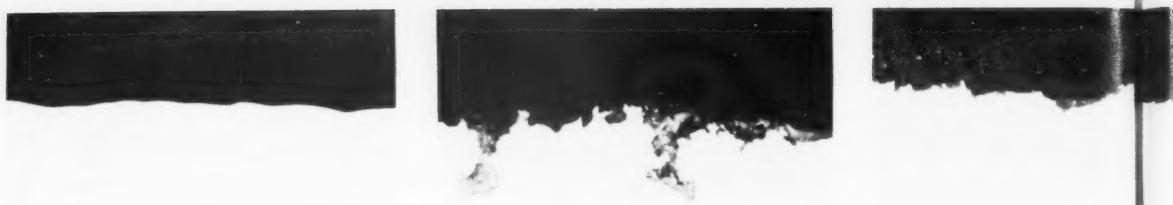
An installation that eliminates the hydrogen-air explosion hazard normally involved in such a use of hydrogen was recently devised by R. M. Carson of NBS.¹ In this system, the inert gas, helium, is used

to purge and flood the hydrogen lines automatically to prevent the admission of outside air in case the internal hydrogen pressure falls below atmospheric pressure. The assembly is basic enough to be adaptable to almost any type of hydrogen gas supply.

In the safety installation, a cylinder of helium is connected in the hydrogen network. The pressure regulator in the helium line is normally set from 10 to 20 pounds lower than that of the hydrogen line. The helium begins to flow only if the hydrogen-line pressure drops to that of the preset pressure of the helium. The hydrogen remaining in the system is then rapidly expelled until fully replaced by the safe helium; and a hazardous mixture of air and hydrogen is never allowed to take place within the potentially dangerous operating chamber.

This installation is being used with complete success in conjunction with hydrogen furnaces, with radiant ovens and radio-frequency heating setups, and with various devices and components treated in hydrogen-filled enclosures.

¹ Now of the Diamond Ordnance Fuse Laboratories, Department of Defense.



Ceramic Coatings for Use in

TO MEET the increasing demand for high-temperature protection of alloys in nuclear reactors, the National Bureau of Standards has developed a ceramic coating material of extremely low thermal neutron absorption coefficient. J. C. Richmond, H. G. Lefort, C. N. Williams, and W. N. Harrison of NBS developed this ceramic material after making an investigation involving over 200 ceramic coating mixtures. Most promising of the materials investigated are boron-free coatings of the frit-refractory type in which a high-barium frit is combined with ceria-chromic oxides. Tests indicate that these coatings which have computed neutron absorption coefficients in the range of 0.15 to 0.50 barns, satisfactorily withstand temperatures in excess of the 1,000° C found in nuclear reactors.

The use of ceramics or metal-ceramic combinations generally offers the only alternative to the use of bare metals for shields, moderators, and fuel rods in atomic piles designed to operate at high temperatures. The nuclear property that chiefly determines the suitability of a ceramic coating for pile construction is its low absorption of neutrons when the material is placed in the path of a neutron beam. The common ceramic coating contains boron, which may be introduced as borax or as boric acid. So far as ceramic considerations are concerned, there is no objection to boron. However, this element has an unusually large neutron capture cross section. A ceramic material assigned for use as a moderator would therefore be quite unacceptable if it contained significant amounts of this element.

Early in the program a goal was established for the maximum value of the absorption coefficient of the ceramic coatings: This value should not exceed that of the alloy to which the coating was to be applied. A survey of published data of the elements indicates that the most commonly used heat resisting alloys have thermal neutron coefficients ranging from 2.5 to 20 barns. On the basis of these data, a value of three barns appeared to be a reasonable maximum to set for the coatings, although it was considered desirable to keep the coefficient as low as practicable. The major constituents in the ceramic coatings were therefore limited to those elements having coefficients of three barns or less; minor constituents were limited to 10 barns or less.

The problem of developing these new coatings was attacked through systematic alteration of the composition of NBS coatings A-417, A-418, and A-19, pri-

marily by eliminating boron with its neutron absorption coefficient of 740 barns. Coating A-417, which contains 70 parts of frit 331, and 30 parts of chromic oxide, was originally developed for the protection of high-temperature alloys such as type 321 stainless steel and Inconel. NBS coating A-418 is similar to A-417 except that, instead of frit 331, it contains frit 332, which is free of beryllium oxide, and for this reason has largely replaced A-417 in commercial use. NBS coating A-19, which contains 80 parts of a groundcoat enamel frit plus 20 parts of alumina, was developed for the protection of low-carbon steel at temperatures up to 1,200° F, but it has also found application for protection of some of the high-temperature alloys at higher temperatures.

During the course of the investigation, frits were designed and smelted in which various oxides were substituted for B_2O_3 in NBS frit 331 (table 1) and its modification, NBS frit 332. The most successful were those in which $Zn_3(PO_4)_2$ and $Ca_3(PO_4)_2$ were substituted for B_2O_3 . Frits containing appreciable quantities of CaF_2 severely attacked the refractory crucibles in which they were smelted, but frits that did not contain either CaF_2 or a phosphate were in general difficult to melt.

Tests of coatings on a number of metals indicate that those containing the newly developed NBS frit 435 were outstanding in the protection they afforded the various alloys; but several hours or days after completion of an extended heating test, these coatings chipped from the austenitic stainless steels to which they were applied. This behavior appeared to be due to stresses produced by differential thermal expansion. To increase the thermal expansion of the frits, TiO_2 was substituted for SiO_2 , GeO_2 for SiO_2 , and FeO for BaO . Increased thermal expansivity of the coatings was also obtained when CeO_2 was used instead of Cr_2O_3 as a refractory admixture with NBS frit 435.

Of the numerous frits that were designed and smelted, the best results were obtained from NBS frit 435 and its modifications. Compositions of the base frit, of NBS frit 435, and of several other boron-free frits are given in table 1. This table also includes the computed average neutron absorptions for the frits, the fritting temperatures, and the softening points by the fiber deformation technique. While the substitution of TiO_2 for SiO_2 increased the softening point as determined by this method, it decreased the fritting temperature.

e | Nuclear Reactors

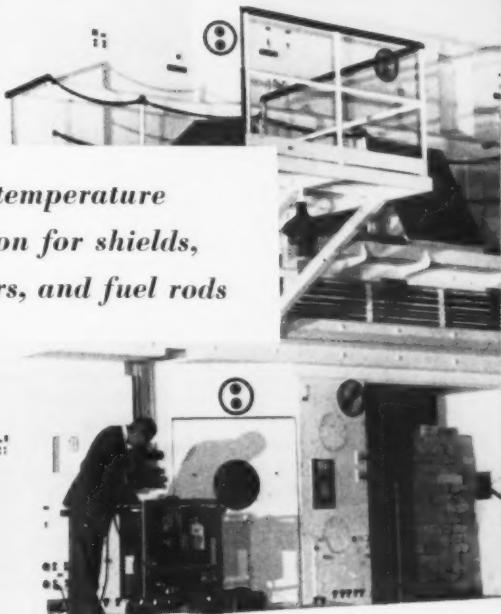
Above: Photomicrographs ($\times 300$) of metallographic sections of specimens of type 310 stainless steel, illustrating the criteria used in the evaluation of attack in the extended heating test. (Left to right by pairs) uncoated metal before and after test, and metal with 2 coats N-89 before and after test. **Background photo right:** Reactor at the National Reactor Testing Station in Idaho (courtesy of AEC). **Below:** Special furnace used in heating and thermal shock tests.



The computed average absorption coefficients for the various frits ranged between 0.15 and 0.25 barns, indicating that the boron-free frits were all satisfactory from this standpoint. The substitution of TiO_2 for SiO_2 increased slightly the neutron absorption of the frits, but it was still below 0.5 barns as compared to 3.0 barns or more for the base metal.

The raw materials used in the production of frits were all in powdered or in fine granular form, and the frits were prepared according to the usual laboratory

high temperature protection for shields, moderators, and fuel rods



procedures. Technical-grade oxides were used if available. When such oxides were not available, not stable in composition, or not readily soluble in the glass, the elements were added in the form of simple stable compounds.

Water suspensions, or "slips," of the 200 coatings studied in this investigation were prepared by grinding in a ball mill a mixture of a frit and a refractory crystalline material with water and clay. The consistency of the slip was adjusted by the addition of water or electrolyte until a coating approximately 1 mil in thickness could be obtained by dipping a metal alloy sample into the slip. The dipped specimens were dried at 220° F and then fired in a furnace for 4 minutes at the appropriate temperature—in the range of 1,850° to 2,250° F. The most promising results have been obtained with coatings which contain cerium oxide or both cerium oxide and chromic oxide as the refractory addition. Tests in which the proportions of frit and refractory were systematically varied indicate that the optimum ratio was in the range of 65 parts by weight of frit to 35 parts by weight of refractory, although good results were obtained with a few coatings in which the proportion was 95 parts frit to 5 parts refractory. Most of

TABLE 1. *Frit compositions in mol percent*

Material	Base frit No. 331	Experimental frit No.—				
		435	452	453	454	455
SiO ₂	50.80	51.02	46.02	43.52	41.02	46.55
TiO ₂			5.00	7.50	10.00	5.00
BaO.....	23.04	25.51	25.51	25.51	25.51	25.77
B ₂ O ₃	7.49					
CaO.....	5.72	6.12	6.12	6.12	6.12	9.28
ZnO.....	4.93	5.10	5.10	5.10	5.10	3.43
Al ₂ O ₃						
ZrO ₂						
BeO.....	8.02	10.20	10.20	10.20	10.20	6.88
P ₂ O ₅		2.04	2.04	2.04	2.04	2.04
Total.....	100.00	99.99	99.99	99.99	99.99	100.00
Average neutron absorption (barns).....	21.7	0.192	0.287	0.334	0.381	0.287
Fritting temperature, °F.....	2125	2600	2530	2460	2150	2150
Softening point, °F.....	1385	1462	1474	1535	1562	1483

the coatings contained 5 parts by weight of enameling clay, used as a flotation agent. The mill batch for coating N-108, given in table 2, is typical of those used. None of the frits that were free of BeO showed promise in this investigation.

Most of the coatings that adhered well (table 3) were tested to evaluate the protection they afforded the various alloys in an extended heating test. In this test, the samples were heated to 1,900° F and cooled to room temperature a number of times in a series of irregular cycles. During the one-week trial, the samples were at the high temperature for a total of 150 hours. Under this test, none of the coatings were outstanding when applied to type 321 stainless steel, but coatings N-89, N-108, N-109, N-146, and N-149 gave appreciable protection. Coatings N-94, N-95, N-141, N-148, and N-151, in addition to the above, appeared to be in good condition at the end of the test on type 309 stainless steel. Most of these coatings, as well as N-70, N-73, N-140, and N-147, performed well when applied to type 310 stainless steel. Most of the coatings also showed good results when applied to Inconel.

Metallographic examination of tested and untested coated specimens revealed that some corrosion occurred beneath the coating in every case in the extended heating tests, but the amount or apparent depth of "stringer" corrosion was markedly reduced by the coating. Photomicrographs showed corrosion to a depth of approximately 1½ mils on uncoated specimens, and to less than half of this depth on specimens coated with N-89. In terms of cross sectional area

TABLE 2. *Mill batch for coating N-108*

Mill 2½ hours in 1-quart ball mill (Approximately 15,000 revolutions of mill)

Material	Parts by weight
grams	
Frit 435.....	195
CaO ₂	75
Cr ₂ O ₃	30
Clay.....	15
Water.....	120

TABLE 3. *Compositions of promising coatings, parts by weight*

Coating	Frit		Refractory, amount		Clay, amount	Firing temperature
	No.	Amount	Cr ₂ O ₃	CaO ₂		
N-70.....	452	70	30.0	...	5.0	2,100
N-73.....	453	70	30.0	...	5.0	2,100
N-89.....	435	95	5.0	...	5.0	2,075
N-90.....	455	95	5.0	...	5.0	1,880
N-94.....	453	65	35.0	...	5.0	2,165
N-95.....	454	65	35.0	...	5.0	2,165
N-108.....	435	65	10.0	25.0	5.0	2,120
N-109.....	435	65	...	35.0	5.0	2,075
N-110.....	435	65	10.0	25.0	5.0	2,100
N-141.....	435	60	...	40.0	5.0	2,050
N-116.....	435	75	...	25.0	5.0	2,050
N-147.....	435	65	2.5	32.5	5.0	2,150
N-148.....	435	65	5.0	30.0	5.0	2,100
N-119.....	435	65	7.5	27.5	5.0	2,100
N-150.....	435	65	12.5	22.5	5.0	2,150
N-151.....	435	65	15.0	20.0	5.0	2,150

^a Wyoming bentonite.

of the stringers caused by corrosion, the difference between coated and uncoated specimens is much greater.

Although none of the coatings so far evaluated by the microscopic method greatly reduced the depth of uniform oxidation that occurs beneath the coating, the depth of stringer penetration was reduced from 1.55 mils on a bare specimen to a minimum of 0.65 mils under coating N-108, and the number of stringers per inch was reduced from 228 to 20.

A series of thermal shock resistance tests was performed on coated specimens of various alloys as well. The coated specimens were heated in a furnace and then quenched by total immersion in water at room temperature. All withstood quenching from 1,100° F, and the best did not fail when quenched repeatedly from 2,000° F. This thermal shock treatment is much more severe than the coatings would normally be expected to encounter in service.

For further technical details, see Ceramic coatings for nuclear reactors, by Richmond, Lefort, Williams, and Harrison, *J. Am. Ceram. Soc.* (in press).

Selected references relating to high-temperature ceramic coatings and porcelain enamels: Recent ceramic coatings for high-temperature alloys, *NBS Tech. News Bull.* **35**, 145 (October 1951); Radioisotope study of cobalt in porcelain enamel, Harrison, Richmond, Pitts, and Brenner, *J. Am. Ceram. Soc.* [5] **35** (May 1952); Migration of cobalt during firing of ground-coat enamels on iron, Harrison, Richmond, Pitts, and Brenner, *NACA Tech. Note 2695* (June 1952); Effect of temperature on the electrical resistivity of several ceramic and silicone-type coatings, Strauss, Richards, and Moore, *Special Tech. Publ. No. 153, Am. Soc. Testing Materials* (1953); Relation between roughness of interface and adherence of porcelain enamel to steel, Richmond, Moore, Kirkpatrick, and Harrison, *NACA Tech. Note 2934* (April 1953), also published in *J. Am. Ceram. Soc.* [12] **36** (Dec. 1953); Galvanic corrosion theory for adherence of porcelain-enamel ground coats to steel, Moore, Pitts, Richmond, and Harrison, *NACA Tech. Note 2935* (June 1953); Investigation of gases evolved during firing of porcelain enamels, Moore and Mason, *J. Am. Ceram. Soc.* [8] **36** (August 1953), also published in *J. Am. Ceram. Soc.* [1] **37** (January 1954); Ceramic coatings for high-temperature protection of steel, Harrison, Moore, and Richmond, *J. Research NBS* **38**, 293 (1947) RP1773.

Cuvette Densitometer

an
improved
instrument
for
the
research
physiologist

THE CUVETTE DENSITOMETER is used in medical practice and research to make a continuous record of the rate of dye dilution in the heart chambers by observing the blood flow from a peripheral artery. From this record, calculations can be made to determine the amount of blood pumped by the heart during each stroke. An improved densitometer developed by S. R. Gilford of NBS, possesses several advantages over previous instruments of this type. Among these are greater stability and sensitivity, smaller size, and greater convenience of application. The development is part of a program on medical instrumentation carried out at the Bureau in cooperation with the Army Medical Service Graduate School.

To the research physiologist, cardiac output is not only an important index of heart function but is also of great interest in studies of the cardio-vascular system. Although there is no direct method of measuring the output of the heart, several procedures have been devised to obtain this information. One method, developed by Stewart¹ and modified by Hamilton,² is based on observation of the rate at which tracer material introduced into the heart chambers is diluted by the flow of blood through the heart. It is then possible to determine the average rate of blood flow if the amount of injected material is known and if the concentration-time function can be measured. In one method, Evan's Blue, an organic dye, is introduced into the heart through a vein, and the diluted material that issues from the heart is sampled at a peripheral artery. The change in concentration of the dye in the blood as a function of time is measured by diverting the blood through a transparent cuvette in which the variations in opacity of the blood can be measured and then recorded with suitable electronic equipment.

Schematic diagram of the improved cuvette densitometer.

One of the serious defects in previous instruments for measuring blood opacity has been instability in electronic circuitry. During the approximately 30 seconds required to record the dye-dilution curve, it is essential that zero and gain be stable. Also, since it is necessary to calibrate the instrument—a procedure which may be delayed by several hours in some instances—it is essential that the sensitivity remain constant for long periods of time. In the design of the NBS cuvette densitometer, therefore, very careful consideration was given to obtaining high stability of sensitivity.

The optical system of the instrument includes a source of monochromatic light for illumination of the cuvette, and a photocell to intercept the transmitted light. A stable light source is obtained by using an incandescent lamp powered by a constant-voltage transformer. A condensing lens collimates the beam of light. The filters which provide the monochromatic light give maximum response to Evan's Blue.

The cuvette brings into the optical path a continuous blood sample about 1.0 mm thick. The optical density of the undyed blood averages about 2.0 to monochromatic light centered at 630 millimicrons, and the dye increases this background density by about 0.1. To assure complete interchange of fluid, the cuvette is designed so as to prevent streaming of the blood flow. Thus, the material in the cuvette is representative of the instantaneous concentration of dye and is not influenced by the previous concentration.

The optical system has an additional feature which permits calibrating the equipment independently of the biological system. A series of neutral-density filters are arranged on a cylinder so that they can be readily introduced into the optical path. It is then possible to check the stability in the operating region with a stable input signal, and to plot the linearity of the output function over the operating range.

¹ G. N. Stewart, *Am. J. Physiol.* **57**, 27 (1921).

² Kinsman, Moore, and Hamilton, *Am. J. Physiol.* **89**, 322 (1929).

The NBS densitometer uses a phototube of the multiplier type to provide the required sensitivity. However, when a photomultiplier tube is used with conventional circuits, cell fatigue may cause variations in sensitivity and baseline stability. This effect is noticeable even when the output current is very low. In the NBS instrument, the effect of cell fatigue is overcome by using a circuit described by Sweet³—a feedback system in which the dynode potentials of the phototube are automatically decreased as the light level is increased. The result is that the circuit tends to maintain a constant output current regardless of the light flux impinging on the photocathode. Thus, the total current drawn from the anode never exceeds one microampere; at this level fatigue is negligible.

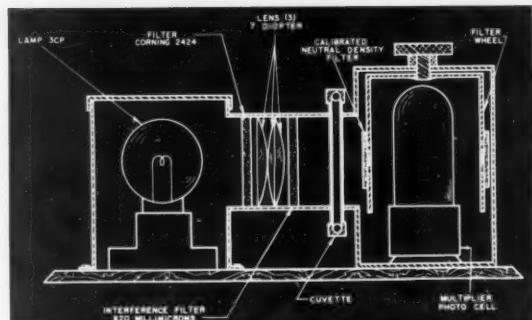
In this circuit, the anode current, normally the output, is kept constant and the dynode divider potential, which is a function of the incident flux, is used as the output. However, the output is not a linear function of the incident flux, but rather the logarithm of this quantity. Since the concentration of the dye is directly proportional to the optical density, and since the logarithmic characteristic of the instrument gives the optical density function, the output of the instrument is directly proportional to the dye concentration.

As the optical density function is a directly additive quantity, the relationship between the output and the concentration remains constant. Thus, a given change in concentration of the dye in the blood produces the same change in output regardless of the background optical density. This is not true for a system with linear response, which gives a progressively decreasing output for equal concentration changes as the background density increases. With the logarithmic function that is incorporated into the NBS instrument, the scale factor does not require readjustment for successive dye injections after the initial determination has been made.

Although the Sweet circuit will measure optical density over a range of at least 0 to 3.0, the NBS densitometer requires only a range of 0 to 0.1. The circuit was therefore modified to include a zero suppression system which is initially adjusted to balance out the output resulting from light transmission through the background density of the undyed blood. Thus, the output can be introduced into an amplifier of sufficient gain to give full-scale recording for maximum density change produced by the dye.

With an output recorder having a full-scale response of 50 microamperes, a density change of 0.07, corresponding to a concentration of Evan's Blue dye of 0.007 mg/cm³, produces a full-scale deflection in the presence of a background density of 2.5. At the same time, the long-term stability of the baseline is about 10 percent of full scale per hour. Superimposed on the long-term drift are short-term random variations which are approximately 3 percent of full scale. Although a record at this sensitivity might be considered noisier than desirable because of these variations, it is quite usable.

³ M. H. Sweet, *J. Soc. Motion Picture Television Engineers*, **54** (January, 1950).



Cross section of the optical assembly of the improved cuvette densitometer.

In actual use such sensitivity is not required, since the maximum dye concentrations encountered in the physiological application are in excess of 0.007 mg/cm³. In the laboratory, sensitivities about $\frac{1}{4}$ of the maximum are used. At these settings, short-term variations are virtually undetectable, and long-term variations present no problem since the determinations are completed in a minute or less.

The components of the cuvette densitometer are divided into two units—the optical assembly in one and the electronic circuitry in the other. The optical assembly is housed in a small wooden carrying case that can be removed when the instrument is in use. In practice it is usually placed near the patient or experimental animal to be studied. The two fluid connections that must be made are standard fittings that are interchangeable with most couplings on medical equipment. The cuvette is readily removed from the system for cleaning and sterilization. The optical assembly with its photocell is coupled to the electronic unit by 12 feet of cable.

The second unit contains not only power supplies and detecting and amplifying circuitry but controls as well. A gain control, which is kept at one setting throughout the experiment, and a zero suppression control, which the operator manipulates until the indicating meter reads zero, are the only electronic adjustments to be made in the normal use of the instrument. The simplicity of control eliminates the need for a high degree of skill and technique on the part of the operator. A set of terminals on the rear of the chassis provides connections to a recording galvanometer.

A number of experiments have been conducted by the Army Medical Service Graduate School to evaluate the performance of the cuvette densitometer.⁴ Comparisons between the dye-dilution method using the cuvette densitometer, and other methods previously established by medical practice indicate that the NBS instrument accurately measures cardiac output.

⁴ Shadie, Ferguson, Gregg, and Gilford, Evaluation of a new cuvette densitometer for determination of cardiac output, *Circ. Res.*, **1**, 200 (May 1953).

For further technical details of the NBS cuvette densitometer, see Gilford, An improved cuvette densitometer, *Rev. Sci. Instr.*, **24**, 696 (August 1953).

Effect of Light on Coated Groundwood Papers

PAPERS containing groundwood fibers, made by disintegrating logs against large grinding stones, are of considerable importance commercially. Newsprint contains about 75 percent groundwood, and other printing papers for use in less permanent types of publications also have large percentages of this fiber.

While groundwood is one of the cheapest paper-making fibers, it is unsuited to many uses because it turns yellow very rapidly when exposed to light. However, some protection from the effects of light is afforded by a clay coating which is frequently added to achieve a better printing surface. This coating consists of very finely divided clay mixed with starch, glue, casein, or synthetic resin as a binder. In an effort to determine the degree of such protection provided to groundwood papers by commercial clay coatings, William K. Wilson and Jack L. Harvey of the Bureau recently made a study of the effect of light on the coated papers. Their work was part of a continuing NBS program on the permanence and degradation of paper.

In addition to coated and uncoated groundwood papers, the NBS investigation included a medium-quality soda-sulfite paper and a good-quality purified sulfite-wood-pulp paper as well as samples of commercial machine-coated papers and papers made in the Bureau's experimental paper mill. Sample sheets were irradiated for 8 hours on each side. The extent of degradation was then determined by physical and chemical measurements on the specimens.

The light source was a carbon arc lamp with a cupric chloride filter and heat exchanger to remove the infrared. The filter light was selected to correspond as closely as possible to skylight filtered by ordinary window glass, but its intensity was considerably higher. Constancy of light dosage was checked by means of a light meter.

Because the light which a paper normally receives is not sufficient to raise its temperature, and because

photochemical reactions are frequently temperature-dependent, the papers were maintained at temperatures between 31° and 33° C during irradiation. The paper was held against a water-jacketed backing plate by drawing air continuously through the sheet. This air stream passed out of the enclosed irradiation chamber in which the backing plate was mounted, circulated in a closed system over a saturated solution of sodium bromide maintained at 30.0° ± 0.2° C in a constant temperature bath, and then returned to the irradiation chamber. The bromide solution maintained the relative humidity at about 57 percent. The water circulating through the aluminum backing was drawn from the constant temperature bath.

The degradation of the coated groundwood papers was compared with that of coated papers containing no groundwood as well as uncoated papers, with and without groundwood. It was found that a clay coating gives considerable protection against the degrading effects of light. In fact, the yellowing of the coated groundwood fibers was only about half that of the uncoated fibers of similar composition. However, groundwood is so light-sensitive that coated groundwood papers are still much less stable than are good quality papers without coating. In general, decoated papers containing groundwood reacted similarly to uncoated groundwood papers, although papers of identical fiber finish were not available for study in both coated and uncoated types.

Under the conditions of the experiments, the coated papers containing no groundwood were not degraded to a measurable extent. In contrast to the groundwood papers, degradation of uncoated papers which contained no groundwood was accompanied by bleaching.

For further technical details, see Effect of light on coated groundwood fibers, by William K. Wilson and Jack L. Harvey, TAPPI 36, 459 (1953).

Publications of the National Bureau of Standards

PERIODICALS

Journal of Research of the National Bureau of Standards, volume 53, number 3, September 1954 (RP2525 to RP2532 incl.). Annual subscription \$5.50.
Technical News Bulletin, volume 38, number 9, September 1954. 10 cents. Annual subscription \$1.00.
CRPL-120. Basic Radio Propagation Predictions for December 1954. Three months in advance. Issued September 1954. 10 cents. Annual subscription \$1.00.

RESEARCH PAPERS

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RP2525. Optical rotations, refractive indices, and densities of dextran solutions. C. F. Snyder, H. S. Isbell, M. R. Dryden, and N. B. Holt.
RP2526. Calorimetric properties of normal heptane from 0° to 520° K. Thomas B. Douglas, George T. Furukawa, Robert E. McCoskey, and Anne F. Ball.
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A property of the normal distribution. Eugene Lukacs and Edgar P. King. The Annals of Mathematical Statistics, (Department of Mathematics, Michigan State College, East Lansing, Mich.) **25**, No. 2, 389 (June 1954).

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Chain block designs with two-way elimination of heterogeneity. John Mandel. Biometrika (52 Hillhouse Avenue, New Haven, Conn.) **10**, 251 (June 1954).

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